OVERVIEW

ARGONNE WORKSHOP ON COMPARATIVE LEACHING BEHAVIOR OF RADIOACTIVE WASTE FORMS

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Received March 18, 1981

INTRODUCTION

To enhance interaction between the various disciplines which are basic to waste management, Argonne National Laboratory in 1979 initiated a series of workshops on fundamental problems in nuclear waste management. This is the second workshop in that series and the topic was chosen for the following reasons.

1. The national radioactive waste program is rapidly approaching the construction of the first waste isolation pilot plant. Because of this it is becoming more and more important to decide on feasible candidates for the waste form, canister, and overpack materials.

2. A great deal of effort has been expended in studies of the fabrication and properties of the various components of the waste package, and this is especially true of the waste form itself. Our decision in arranging this workshop was to concentrate on comparing only this one component since we felt that the waste form was the first and perhaps most important barrier between the radioactivity and man.

3. The most studied waste matrix has been glass, but during recent years crystalline and ceramic materials have received ever increasing attention. Until now, there has been little opportunity to compare the behavior of the various matrices. Therefore, we specifically asked our speakers to concentrate on a single parameter, the leaching behavior under repository conditions. It was felt that this was the most important parameter and was the most readily quantifiable. We realize that the cost and ease of fabrication and feasibility of quality control will be other important considerations in the final choice. Since there is no way of evaluating those parameters until engineering test facilities are operating, we did not include them in our discussions.

The 60 participants at the workshop had interests ranging from general problems in radioactive waste management to specific programs on solid waste forms. It was generally agreed that there were more similarities than differences in behavior of the various forms.

Each of the first five papers (in the symposium) is a summary of the research on a single waste form. The remaining papers each address a specific facet of leaching experiments.

SUMMARY OF THE ARGONNE WORKSHOP PANEL DISCUSSION ON COMPARISON OF WASTE FORM LEACHING BEHAVIOR

The second day of the workshop was occupied with a panel discussion on comparisons of leaching behavior.

Panel Members:

Lynn Boatner
Oak Ridge National Laboratory

Herbert Diamond
Argonne National Laboratory

Michel Maurette
Orsay Campus, University of Paris, France

Joseph Simmons
Catholic University, Washington, D.C.

Raymond P. Turcotte
Battelle Pacific Northwest Laboratories

William B. White
The Pennsylvania State University

George G. Wicks
Savannah River Laboratory

Chairmen:

A. Friedman
M. Seitz
Argonne National Laboratory

The members of the panel emphasized several points. We will summarize them here along with a condensation of the remarks concerning them.

1. Leaching rates for all waste forms were the same within an order of magnitude.

   a. This was only true at temperatures between 80 and 100°C. This is the regime expected for leaching if the overpack canisters resist corrosion for at least 300 years.

   b. There was not enough data to state whether the leaching behavior was dependent on aging or loading of wastes; however, these effects were thought to be unimportant over a wide range.

   c. It is important to determine the dependence of leaching behavior on matrix composition, especially for the crystalline materials. In this latter case quality control will be more difficult and matrix variations more common.

   d. Using a real (i.e., BET) surface area rather than the initial geometric area for rate calculations ($g \cdot m^{-2} \cdot day^{-1}$) probably will be confusing since the real surface area certainly changes during leaching. However, it was felt that a thorough study of changes in surface area and other surface conditions was important and had not been done.

2. Radiation effects on the leaching process may be the most important unanswered problem in radioactive waste management.

   a. *Recoil atom lattice displacements*: A well-known technique for dating geological samples is to count alpha-particle or recoil atom tracks in natural glasses or crystalline materials. This is easily accomplished since these materials preferentially etch along the track path. The same type of preferential etching should occur in waste form matrices. However, a test at Pacific Northwest Laboratory (PNL) using ^{242}Cm-loaded waste glass showed no preferential leaching. It was felt that this problem should be investigated further.

   b. *Radiation-induced pH changes*: It was pointed out that under appropriate conditions H^+ ions are formed in solutions by a radiation field. At PNL, the buildup of HNO_3 in aerated solutions was measured and it was shown that this could affect the leach rate of glasses by dissolving the protective gel layer. This acid build up was thought to be more important for nonflowing systems. It was also thought that backfill materials should contain pH buffers to compensate for this effect. Panel members also noted that increases in H^+ concentrations could affect the canister and overpack corrosion rate.

   c. *Radiation-induced oxidation or reduction of waste components*: During the interaction of radiation with water, short-lived reducing (H_2O^-) and oxidizing (OH, HO_2^-) species are formed. These may interact with and change the oxidation state of multivalent waste species. This could mean a large change in the chemistry, solubility, and migration rate of those waste species. Unlike the alpha recoil radiation effect that can occur in the isolated waste cylinder and the pH effect that occurs in the solution away from the waste form, the oxidation (or reduction) will mainly occur at the solution-solid interface in the presence of the radiation field.

The panel came to the following conclusions:

1. Under limited conditions the leaching behavior of all waste forms appeared suitable. The choice of which waste form to use probably would be based on cost and ease of fabrication and quality control.

2. It is important to study the sensitivity of leach rate to changes in composition of the matrix for all forms.

3. It is of great importance of obtain comparisons of the behavior of each waste form under each of the three radiation effects. In fact, it was felt that these effects might provide the major differentiation between waste forms.